A COMPARISON OF SIMULATED DISTILLATION TO TRUE BOILING POINT DISTILLATION OF H-COAL® DISTILLATES

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INTRODUCTION

A very important characteristic of liquid hydrocarbons derived from either petroleum or synthetic fuel feedstocks is the boiling point distribution. In many plant operations, all yield calculations, material balances, physical property correlations, and computer process simulations are based upon the true boiling point (TBP) distillation curve of the streams in question. Until the advent of simulated distillation, there were two basic methods for determining the TBP distillation for a sample: (1) to actually perform a TBP distillation, which is a time cor suming procedure (usually a minimum of eight hours), or (2) to perform : single theoretical plate distillation (designated by the American Society for Testing and Materials as Method D-86[1] for atmospheric distillations, and Method D-1160[2] for vacuum distillations), and converting the data to TBP by mathematical correlations. With the introduction of simulated distillation by gas chromatography (designated ASTM D-2887[3]), a method, which offers a relatively short analysis time of approximately one hour, became available to the analyst. The validity of the use of simulated distillation for H-Coal® liquids has been questioned due to the presence of oxygenated compounds and large concentrations of aromatic components. The objection to the use of simulated distillation for the analysis of highly aromatic oils, such as those derived from coal liquefaction processes, is that the indicated boiling points of pure multiple ring components as determined by simulated distillation will differ substantially (20 to 100°F) from the pure component boiling points. ASTM D-2887 suggests that this is due at least in part to different behavior of the vapor-pressure-temperature relationship for aromatic compounds as compared to other hydrocarbon types. One notes, however, that all of the components mentioned by the ASTM method do not contain any multiple ring aromatic compounds that have alkyl substituent groups. The purpose of this paper is to examine a comparison of simulated distillation to TBP derived from both actual TBP distillations and single theoretical plate distillations converted to TBP for various H-Coal® distillates.

EXPERIMENTAL

The true boiling point distillation data presented was obtained using a Todd® distillation column, having fifteen (15) theoretical plates and a five to one reflux ratio. The overhead material was measured on the basis of true weight percent, i.e., the weight of overhead material was compared to the weight of material originally charged to the distillation. The distillation was carried out under atmospheric conditions as much as possible, with vacuum being applied as necessary to prevent thermal decomposition (cracking). The single theoretical plate distillations were performed as per their respective ASTM method. The methods used to convert the single theoretical plate distillation data to TBP data are those outlined in the American Petroleum Institute Technical Data Book. The method used to convert ASTM D-86 data to TBP data was API procedure 3A1.1[4]. In the case of ASTM D-1160 distillations, the procedure was more complex, resulting from the additional variable of vacuum. Any distillation data not carried out at 10 mm Hg was first converted to distillation data at 10 mm Hg using API procedure 5A1.8[5]. The ASTM D-1160 distillation data at 10 mm Hg was then converted to TBP data at 10 mm Hg using API procedure 3A1.2[6]. The resulting TBP data at 10 mm Hg was converted to TBP data at 760 mm Hg using API procedure 5A1.13[7].

All simulated distillation data presented was obtained using a Hewlett Packard® 5731 gas chromatograph equipped with dual flame ionization detectors. The columns used were 10% UCW-982 on Chromasorb PAW (20 inches in length, 1/8 inches in diameter), with the temperature of the column oven programmed from -50°C to 350°C at a rate of 8°C per minute, during the analysis. Calibration for the simulated distillation was based upon normal paraffin hydrocarbons (nC_2 to nC_{44}). Calculations were performed as per ASTM D-2887 using a Mod Comp® computer. Since the response of a flame ionization detector is proportional to the number of carbon atoms present, it is assumed simulated distillation data obtained using this type of detector closely approximates weight percent data. Additional deviations may occur with the presence of heteroatom compounds, however, it is felt that the resulting data will be closer to weight percent data than any other method of reporting. With this in mind, all TBP data were expressed in weight percent. Measurements from the direct TBP distillation were taken in weight percent, and the volume percent single theoretical plate distillation data was converted to weight percent data using a least squared regression developed by Hydrocarbon Research, Inc. which relates density to boiling points for H-Coal® liquids derived from Illinois #6 coal[8].

RESULTS AND DISCUSSION

In order to make a comparison of simulated distillation data to true boiling point distillation data, a definition of TBP data is in order. The ideological concept of a TBP curve results from a plot derived from a complete compositional analysis of the sample and the pure component boiling points of the individual components. For a simple mixture, this plot would be a series of plateaus, resulting in a plot that increases in a step-like manner as the temperature increases. As the number of components in the mixture increases, the step-like nature of the plot decreases, until with an infinite number of components, the plot becomes a smooth curve. For very complex mixtures, the complete compositional analysis required for plotting this type of TBP curve is practically impossible for routine samples. The alternative to this type of TBP curve is one determined empirically by plotting the overhead temperature versus weight or volume percent of material condensed in a batch distillation in which the number of theoretical plates and reflux ratio is set such that an increase of either will produce no significant deviations of the data. This empirically determined TBP curve may deviate substantially from the ideological type of TBP curve due to the formation of minimum or maximum azeotropes. In addition to azeotrope formation, the single theoretical plate distillation technique suffers from inadequate separation.

Since it is practically impossible to compare simulated distillation data to ideal TBP data, due to the extremely complex mixtures found in these liquids, the only alternative is to compare simulated distillation data with the empirically determined TBP distillation curve. Figure 1 compares the distillation curves obtained by direct weight percent TBP distillation and simulated distillation for a full range H-Coal® syncrude. Due to limitations inherent in the single theoretical plate distillation arising from the minimum or maximum overhead temperature allowed, comparisons of the boiling point distribution of fractions were made. Figures 2, 3, and 4 compare boiling point curves for H-Coal® naphtha (IBP to 400°F fraction), H-Coal® middle distillate (400-650°F fraction), and H-Coal® heavy distillate (650°F plus fraction). In order to compare simulated distillation data with weight percent TBP data, the minimum, maximum and average deviations between the two types of analyses and replicate analyses via the same method were computed (see Table I). Since all distillations, with the exception of the direct TBP distillation were performed in duplicate or triplicate, the deviations between the types of analyses were based upon average values for each boiling point. One notes that in all cases, the deviation values calculated for replicate simulated distillation data are lower than the deviation values calculated for replicate TBP data. It is also noted that the maximum and average deviations between the average simulated distillation data and the average TBP data is smaller than the deviation for replicate TBP analyses in all cases except for the naphtha fraction. It is felt that the larger deviation of the naphtha fraction boiling point curves is due to the inadequate separation inherent in single theoretical plate distillations. It is also observed that for the direct TBP distillaton, the greater deviations occurred when vacuum was applied to the system. This observation is consistent with the fact that a small change in a reduced pressure boiling point will magnify when converted to an atomospheric pressure boiling point. As a result, from the examination of the distillation data it becomes apparent that simulated distillation data compares favorably with weight percent distillation data, whether derived from direct TBP distillation or single theoretical plate distillation data and converted to TBP data.

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3. ibid, Part 24, D-2887

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6. ibid, 3A1.2

7. ibid, 5A1.13

8. H-Coal® Data Book, First Issue, Prepared for US Energy Research and Development Administration, (Revised Contract No. EF-01-75-1544). Hydrocarbon Research, Inc. and HRI Engineering, Inc., 1976.

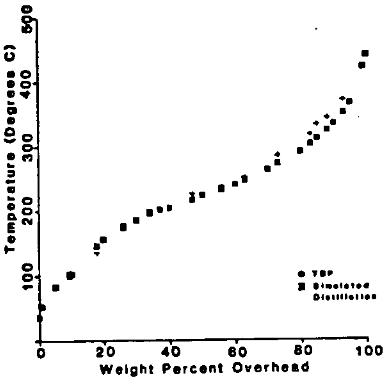

FIGURE 1 - Comparison of the TBP distillation curve (wt.%) to the simulated distillation curve of a full range H-Coal® Syncrude.

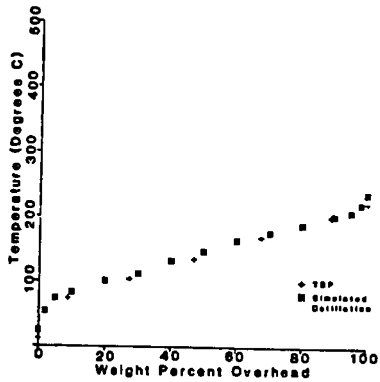

FIGURE 2 - Comparison of the TBP distillation curve (wt.%) to the simulated distillation curve of an H-Coal® Naphtha.

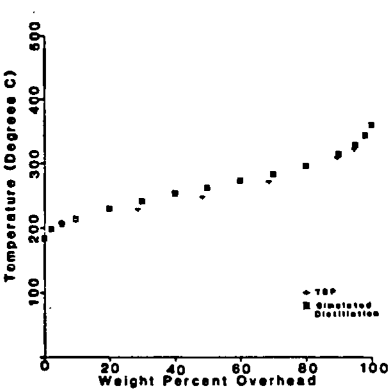

FIGURE 3- Comparison of the TBP distillation curve (wt.%) to the simulated distillation curve of an H-Coal® Middle Distillate

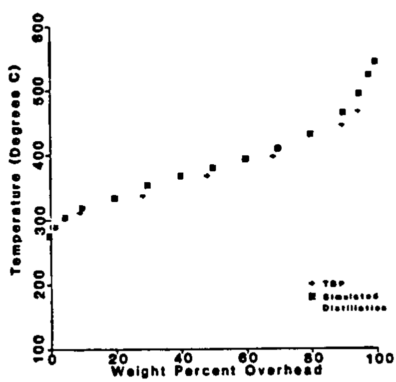

FIGURE 4 - Comparison of the TBP distillation curve (wt.%) to the simulated distillation curve of an H-Coal® Heavy Distillate

TABLE I

COMPARISON OF SIMULATED DISTILLATION

DATA TO TBP DISTILLATION DATA

		Deviation Between Replicate Analyses: TBP	Deviation Between Replicate Analyses: Simulated Distillation	Deviation Between Avg. TBP and Avg. Simulated Distillation
H-Coal® Syncrude[1]	Minimum	--	±0.5°C	±1.5°C
	Maximum	--	±6.7	±11.0
	Average	--	±1.5	±5.5
H-Coal® Naptha[2] IBP-400°F Fraction	Minimum	±0.0°C	±0.0°C	±0.5°C
	Maximum	±2.5	±1.5	±8.0
	Average	±0.9	±0.3	±4.1
H-Coal® Middle Distillate[3] 400-650°F Fraction	Minimum	±0.0°C	±0.0°C	±1.0°C
	Maximum	±9.0	±0.5	±7.0
	Average	±4.5	±0.2	±4.0
H-Coal® Heavy Distillate 650°F Plus Fraction	Minimum	±1.0°C	±0.0°C	±2.0°C
	Maximum	±13.0	±3.5	±7.0
	Average	±4.7	±1.6	±4.2

[1] Analysis determined by direct TBP distillation.

[2] Analysis determined by ASTM D 86 distillation, with data converted to weight percent TBP.

[3] Analysis determined by ASTM D 1160 distillation, with data converted to weight percent TBP.